Progress in Surface Science, Vol. 24(1-4), pp. 1-282, 1987
Printed in the U.S.A. All rights reserved.
0079–6816/87 $0.00 + .50
Copyright © 1987 Pergamon Journals Ltd.

OPTICAL PROBES OF ORGANIC THIN FILMS: PHOTONS-IN AND PHOTONS-OUT

M.K. DEBE

Corporate Research Laboratory, 3M Company
St. Paul, MN 55144

Abstract

This monograph attempts to present a comprehensive review of the current applications and characteristics of photon-in, photon-out optical techniques used to characterize organic thin solid films and their interfaces. The optical probes are grouped according to their common origins within the point dipole approximation and both theoretical aspects and experimental capabilities and limitations are discussed. Emphasis is given to describing how information about the surface and interface characteristics, the thin film microscopic physical structure and the macroscopic optical properties derives from nine basic optical approaches used in some two dozen different experimental configurations. The recent literature for each configuration is surveyed to illustrate the type and extent of information retrievable, and also the realistic limitations. The nine basic optical methods include spectrophotometry, ellipsometry, microscopy, emission, X-ray scattering, surface electromagnetic wave spectroscopy, infrared spectroscopy, Raman spectroscopy and non-linear optical approaches. The level of presentation is directed at nonexperts in the multidisciplinary research and technology fields which utilize organic thin films in the submonolayer to micron thickness range.

Contents

1. Introduction 5
2. General Properties 8
   A. Dipole origins of the three main classes
   B. Experimental characteristics for comparison 13
   C. Polarization, Fresnel coefficients and the Kramers-Kronig relation 16
      (i) Polarization properties 16
      (ii) The Fresnel coefficients 19
      (iii) The Kramers-Kronig relations 21
3. The Linear Dipole Techniques - Primarily Electronic Origin 23
   A. Spectrophotometry 23
      (i) Transmission only possible 24
      (ii) Reflection and transmission both possible 30
      (iii) Surface reflectance and modulation spectroscopies 34
      (iv) Photoluminescence 44
   B. Ellipsometry 54
      (i) Introduction 54
      (ii) Experimental considerations 55
      (iii) Relating Δ and ψ to the film properties - the importance of modelling 59
      (iv) Applications to organic thin films 68

C. Microscopy and interferometry 78
(i) Crossed polarizer microscopy 79
(ii) Optical interferometry 81
D. X-ray scattering and diffraction 83
(i) Introductory ideas 84
(ii) Grazing incidence scattering (GIS) 87
(iii) Transmission x-ray diffraction 94
(iv) EXAFS and XANES 95
E. Surface electromagnetic wave techniques - electronic and vibrational 97
(i) Introduction 97
(ii) SEW experimental configurations 100
(iii) Some basic elements of surface plasmon polaritons 105
(iv) Applications to organic overlayers 111
F. Integrated optics approaches 126
4. The Linear Dipole Techniques - Vibrational Origins 128
A. Transmission IR spectroscopy 128
(i) Introduction 128
(ii) Fundamentals of IR absorption 129
(iii) Fourier transform vs. dispersion spectrometers 133
(iv) Sensitivity limits and extracting physical information-some examples 134
B. External reflection-absorption IR spectroscopy 137
(i) Introduction 137
(ii) Experimental and theoretical aspects 139
(iii) Extracting thin film structure information 152
(iv) Applications to organic overlayers 170
C. Multiple internal reflection spectroscopy 179
(i) Introduction 179
(ii) Optical field configuration in the evanescent region 181
(iii) Applications to very thin films 186
D. Other configurations 191
(i) IR emission 191
(ii) EMIRS and SNIFTIRS 193
(iii) SEW and DRIFT 194
E. Surface Brillouin scattering 195
5. The First Order Induced Dipole Techniques 199
A. Unenhanced surface Raman 201
(i) Experimental configurations 201
(ii) Extracting orientation information 203
(iii) Specific applications of UER 211
B. Enhanced Raman spectroscopy 213
(i) Resonance Raman 213
(ii) SEW enhanced Raman 216
(iii) Waveguide enhanced Raman 217
(iv) Surface enhanced Raman spectroscopy 220

6. The Second Order and Higher Non-Linear Polarization Techniques 232
A. NLO background 232
B. Surface second harmonic generation 237
(i) Surface SHG on insulating substrates 238
(ii) Spectroscopic second harmonic generation 246
(iii) Metal and semiconductor surfaces - smooth and rough 249
(iv) SEW and waveguide enhanced SHG 253
C. Higher order non-linear optical probes 255
D. Conclusions 258
7. Conclusions and Final Comments 259
Acknowledgements 260
References 261

Notations

μ - molecular dipole moment
N - complex refractive index
n - real part of the refractive index
k - imaginary part of the refractive index
R_i - reflectance from an interface ($i = p$ or s)
T_i - transmittance through an interface ($i = p$ or s)
λ - wavelength
p - in-plane polarized
s - out-of-plane polarized
ΔR - change in reflectance of a surface with and without an overlayer
ΔT - change in transmittance of a surface with and without an overlayer
ν - frequency
$\bar{\nu}$ - wavenumber
ω_p - plasma frequency
ω - angular frequency
ϵ_j - complex dielectric constant of medium j
$\boldsymbol{Q}$ - x-ray diffraction momentum transfer
$\boldsymbol{k}$ - electromagnetic wave momentum vector
$r_{1,2}$ - Fresnel reflection coefficient for a 2 phase system
r_{123} - Fresnel reflection coefficient for a 3 phase system
d - film thickness
ρ - r_p/r_s, ratio of Fresnel reflection coefficents
ψ - ellipsometric parameter relating amplitude change of p and s waves
Δ - ellipsometric parameter relating phase change of p and s upon reflection
Ψ - polarization state
f_v - void fraction
$k_{\|}$ - surface parallel momentum vector
$k_{\perp}$ - surface normal momentum vector
ϵ' - real part of ϵ

ε'' - imaginary component of $\boldsymbol{\varepsilon}$
k_{sp} - surface plasmon momentum vector
θ_p - critical angle for SEW spectroscopy
R_p - p-polarized reflectivity
R_s - s-polarized reflectiviity
$\boldsymbol{P}$ - induced dipole moment
$\boldsymbol{\alpha}$ - polarizability tensor
$\boldsymbol{E}$ - electric field vector
Q_i - vibrational normal coordinate
α_{pq} - polarizability matrix element
$\chi^{(n)}$ - n^{th} order susceptibility tensor
$\beta^{(n)}$ - n^{th} order molecular polarizability
β_{ijk} - hyperpolarizability tensor element
Ω - acoustic phonon frequency
$\boldsymbol{q}$ - acoustic phonon wavevector

Abbreviations

ATR - Attenuated Total Reflection
CARIS - Constant Angle Reflection Interference Spectrum
CARS - Coherent Anti-Stokes Raman Scattering
DR - Differential Reflectance
EM - Electromagnetic
EMIR - Electrochemically Modulated IR
ES - Ellipsometry
EXAFS - Extended X-ray Absorption Fine Structure spectroscopy
FL - Fluoresence
FT - Fourier Transform
FTIR - Fourier Transform IR
GIS - Grazing Incidence Scattering
IR - Infra-red
IRE - Internal Reflection Element
IRRAS - Infra-red Reflection Absorption Spectroscopy
IRS - Internal Reflection Spectroscopy
LB - Langmuir-Blodgett
MIR - Multiple Internal Reflection
NL - Nonlinear
NLO - Nonlinear Optics
PEM - Photo elastic modulator
RAIR - Reflection Absorption IR
RR - Resonance Raman
SCARS - Surface CARS
SE - Spectroellipsometry
SEL - Surface Enhanced Luminescence
SERRS - Surface Enhanced Resonance Raman Spectroscopy
SERS - Surface Enhanced Raman Spectroscopy
SEW - Surface Electromagnetic Wave (spectroscopy)
SHG - Second Harmonic Generation
SNIFTIR - Subtractively Normalized Infrared Fourier Transform IR